

Peroxides. IV.² Aliphatic Diperacids

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A previously unreported series of peroxides, the C₅-C₁₀ and the C₁₂ and C₁₆ α,ω -diperacids, have been prepared in high yield from the corresponding dibasic acids and 65% aqueous hydrogen peroxide in concentrated sulfuric acid solution. The products were characterized by peroxide oxygen content, X-ray diffraction, polarography and ultimate analysis. The long-spacings of the odd and even diperacids fall on a single line and the angle of tilt is essentially the same as that of dibasic acids, the C-form of aliphatic monocarboxylic acids and the C₉-C₁₆ aliphatic monoperacids. Polarograms of the diperacids are similar to those of monoperacids previously described except that the diffusion current constant is only 1.6 times as great.

In contrast to organic monoperacids, of which

numerous well-characterized examples are known^{3,4} diperacids are almost completely unknown. Bae-

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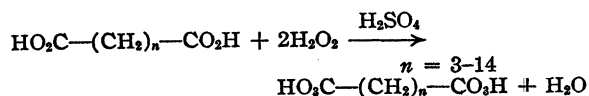
(2) Paper III is THIS JOURNAL, **77**, 5537 (1955).

(3) W. E. Parker, C. Ricciuti, C. L. Ogg and D. Swern, *ibid.*, **77**, 4037 (1955).

(4) D. Swern, *Chem. Revs.*, **45**, 1 (1949).

yer and Villiger⁵ and Milas and Panagiotakos⁶ reported the preparation of diperterephthalic and diperoxalic acids, respectively, by the reaction of the appropriate acid chloride with hydrogen peroxide, but the products isolated in low yield were not characterized.

In a previous publication,⁷ we described a procedure for preparing aliphatic monoperacids in high yield directly from the carboxylic acid and 50–65% hydrogen peroxide in concentrated sulfuric acid solution. This reaction has now been applied to the C₅ through C₁₀ and the C₁₂ and C₁₆ α,ω -dicarboxylic acids to produce the corresponding aliphatic diperacids in good to almost quantitative yield.



For best results, four moles of hydrogen peroxide (100% excess) are employed per mole of dibasic acid. Three hours reaction time is required for the preparation of the C₅–C₁₀-diperacids and 5 hr. for the longer chain members.

Diperglutaric and diperadipic acids have a substantial solubility in water. They are isolated by diluting the reaction mixtures with saturated ammonium sulfate solution at 0° followed by filtration. The higher diperacids are precipitated by dilution with a half-saturated ammonium sulfate solution. Dipersuccinic acid could not be precipitated from the reaction mixture because of its high solubility even in saturated ammonium sulfate.

Analytically pure samples of dipersuberic and higher diperacids are obtained from the reaction products by recrystallization of the reaction products at 0° from ethanol–water mixtures. The shorter-chain compounds are recrystallized from water. In general only fair yields (60%) of analytically pure products are obtained as a result of a combination of high solvent solubility and hydrolytic decomposition. Temperatures in excess of 45° should be avoided in recrystallization; otherwise most of the peracid decomposes. To reduce the time of contact between diperacid and warm solvent and to keep decomposition at a minimum, the solvent is heated to 40–45° prior to addition of the compound. This is particularly important in large-scale recrystallizations.

The diperacids prepared in this study are soluble in 95% ethanol, acetone, ether and dioxane and insoluble in hydrocarbons. The shorter chain (C₅–C₇) members are soluble in water.

Analytically pure diperacids have variable melting-decomposition temperatures of about 80–100°. It is doubtful that these are true melting points since they are not reproducible and gas evolution is observed in the liquid mass. At room temperature, however, the diperacids are relatively stable and they are not shock-sensitive. For long-term storage they should be kept in the refrigerator. They are flammable and are consumed rapidly and

completely (no carbonaceous residue) when plunged into a flame.

The pure diperacids were characterized by ultimate analysis, peroxide oxygen content, polarographic examination and X-ray diffraction. Dipersebic acid was titrated potentiometrically in aqueous alcohol as rapidly as possible and gave a neutralization equivalent corresponding to two acid groups (percarboxyl) per mole. The point of inflection in the titration curve was two pH units higher and the *pK* value three pH units higher than those obtained with sebic acid. This result parallels that obtained in comparing monoperacids with the corresponding carboxylic acids.⁸

Polarograms of the diperacids are essentially the same as those of the monoperacids.⁸ The half-wave potential is at the same position but the diffusion current constant is only 1.6 times that of the monoperacids. The polarograph can be used for analysis of the diperacids, but for routine work it is more convenient to use a standard iodometric method with a modified solvent system (see Experimental).

Long-spacings were obtained on the C₅–C₁₀-diperacids, and the results were compared with those obtained on the corresponding dibasic acids and on the monoperacids and carboxylic acids reported previously.⁷

The long-spacings of the diperacids increase regularly as the hydrocarbon chain increases. The long-spacings of the even and odd numbered diperacids do not fall on separate lines, as is the case with the corresponding dibasic acids.^{7,8} The long-spacings of the even and odd numbered monoperacids also fall on a straight line.

Figure 1 is a plot of the long-spacings of diperacids and dibasic acids. The plot of the long-spacings of the diperacids is approximately parallel to that of the C₃ and higher dibasic acids containing an even number of carbon atoms. The long-spacings of the diperacids are about 1 Å. larger than those of the corresponding even dibasic acids. The long-spacings of monoperacids and the corresponding monocarboxylic acids show a similar difference.

The average increase in long-spacing for each additional carbon atom in the diperacid chain is about 1 Å., which is lower than the expected projected distance (1.27 Å.) of one C–C bond. This value of projected C–C distance is extremely close to the value found in the dibasic acids, the C-form of the monobasic acids, and the C₉–C₁₆-monoperacids. Thus, all of these compounds crystallize with essentially the same angle of tilt.

We were unable to obtain a powder pattern of diperadipic acid that had a long spacing different from that of adipic acid although the side spacings were different.

Experimental

Starting Materials.—The C₄–C₁₆-dibasic acids were Eastman White Label Organic Chemicals. 1,10-Decanedicarboxylic and 1,14-tetradecanedicarboxylic acids were obtained from the Aldrich Chemical Co. The former had the correct melting point and was used as received. The latter

TABLE I
ALIPHATIC DIPERACIDS

Diperacid	Reactants, ^a grams		Yield of diperacid, ^b %	Recrystallized products ^c				Hydrogen, % ^d	
	H ₂ SO ₄ (95%)	H ₂ O ₂ (65%)		Peroxide oxygen, % Calcd.	Peroxide oxygen, % Found	Carbon, % ^d Calcd.	Carbon, % ^d Found	Calcd.	Found
Diperglutaric (C ₈)	60	32	20	69	19.5	18.4	36.6	4.88	5.15
Diperadipic (C ₆)	25	14	10	64	17.9	17.0	40.4	5.62	6.12
Diperpimelic (C ₇)	25	13	10	98	16.6	16.4	43.7	6.24	6.36
Dipersuberic (C ₈)	11	5	3.6	90	15.5	16.0	46.5	6.78	7.05
Diperazelaic (C ₉)	25	11	10	80	14.5	14.4	48.8	7.20	7.69
Diparsebacic (C ₁₀)	30	10.5	10	82	13.6	13.6	51.2	7.75	7.88
1,10-Decanedipercarboxylic (C ₁₂)	20	4.6	5	96	12.2	11.3
1,14-Tetradecanedipercarboxylic (C ₁₆)	13	3.1	4.3	80	10.0	8.0 ^e

^a Reaction time was 3 hr. except for C₁₂- and C₁₆-diperacids, 5 hr. ^b Calculated by multiplying the purity of the crude reaction product by the percentage yield. Purity of crude diperacids usually exceeded 90% except the C₁₆. ^c Recrystallized from water-alcohol mixtures, except for C₈-, C₉- and C₇-diperacids which were recrystallized from water. ^d Because of flashing considerable difficulty was experienced in obtaining good checks. ^e A purer product could not be isolated.

was crystallized twice from 95% ethanol before use. Its melting point was raised to only 120° (lit. 126°). The 65% hydrogen peroxide was generously furnished by J. G. Wallace, E. I. du Pont de Nemours and Co. The 50% commercial grade is also satisfactory.

Diparsebacic Acid.—The preparation of this compound is typical. Ten grams (0.05 mole) of sebacic acid was dissolved in 30 g. of 95% sulfuric acid in an open beaker. With good stirring, 10.5 g. (0.2 mole, 100% excess) of 65% hydrogen peroxide was added dropwise over a 5–10 minute period while maintaining the internal temperature at 20–25° by an ice-water bath.⁹ Stirring was continued for an additional 3 hr. Several volumes of a half-saturated aqueous solution of ammonium sulfate (35 g./100 g. H₂O) were added at 0° and the precipitate of diparsebacic acid was filtered off. The product was washed on the funnel with the cold ammonium sulfate solution until the filtrate was free of sulfuric acid (several washes). Alternatively the precipitated reaction product was dissolved in ether and washed acid-free with ammonium sulfate solution. (This procedure resulted in a large loss of product with the shorter-chain diperacids.) The crude product was dried under vacuum at room temperature; yield 10 g. (85%) and 96% purity. Recrystallization from ethanol-water (1:5) yielded an analytically pure product (70%), neutralization equivalent 113 (calcd. 117). Additional analyses are given in Table I.

Other Diperacids.—The C₈–C₉-diperacids were prepared similarly; the C₁₂ and C₁₆ required 5 hr. reaction time. Purity of crude reaction products exceeded 90% except that of the C₁₆ (only 80%). A saturated ammonium sulfate solution at 0° was required to precipitate diperglutaric and diperadipic acids in yields exceeding 70%. Details and analyses are given in Table I.

Iodometric Analysis.—Purity of the diperacids was determined iodometrically.¹⁰ Water-acetic acid (1:5) was used instead of acetic acid-chloroform (3:2) as the solvent system.

Polarographic Behavior.—The procedures have been reported.^{9,11}

(9) The reaction is highly exothermic. A safety shield should be employed and the operator should wear safety glasses.

(10) D. H. Wheeler, *Oil and Soap*, **9**, 89 (1932).

(11) C. O. Willits, C. Ricciuti, H. B. Knight and D. Swern, *Anal. Chem.*, **24**, 785 (1952).

X-Ray Diffraction.—Long spacings were obtained with a General Electric XRD-3¹² direct recording unit using filtered CuK α radiation (λ 1.5405 Å.), 1° beam slit, 0.1° detector slit, high resolution soller slit, scanning speed 2°/min., chart speed 60 in./hr. linear scale, 4 sec. time constant. To prepare the diperacids for X-ray examination, they were

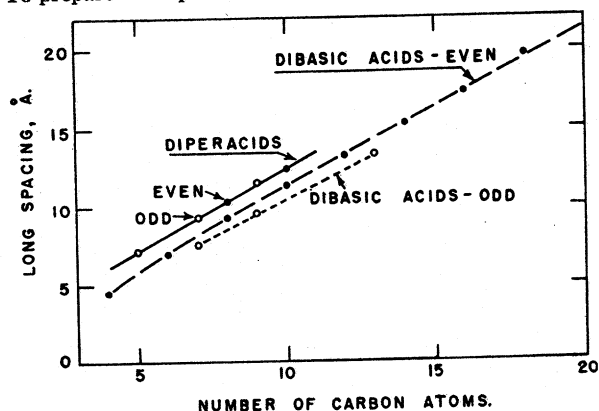


Fig. 1.

dissolved in a minimum amount of ethanol, and the solution was evaporated to dryness at room temperature. All samples were stored at 0° until examined. The samples were gently ground in an agate mortar and mounted in a recessed plastic holder. Long spacings (Å) were as follows: C₆, 7.19; C₇, 9.30; C₈, 10.39; C₉, 11.47; C₁₀, 12.27.

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(12) Mention of a specific instrument does not imply endorsement by the Department of Agriculture over similar instruments not mentioned.